Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan

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Aquatic organisms metabolize arsenic, forming non-toxic arsenic-containing ribofuranosides and arsenobetaine from arsenate. The metabolism results in the occurrence of thermodynamically unstable arsenite and methylarsenicals in natural waters. We studied the seasonal variations of arsenical species in the mesotrophic northern and eutrophic southern basins of Lake Biwa in Japan. The total arsenic concentration in the euphotic zones remained constant in the northern basin, while it was increased by 2-4 times in the southern basin in summer. Despite the larger biomass, the percentage of methylarsenicals was lower in the southern basin. These results indicate that the eutrophication may alter the concentration and speciation of trace elements in the hydrosphere.

Keywords: Arsenate/ Arsenite/ Methylarsenicals/ Ferromanganese oxides/ Aquatic organisms

Lake Biwa is the largest lake in Japan and located in the center of Honshu (Fig. 1). The lake is a source of water supply for the fourteen million people living in the Kansai area and supports many kinds of aquatic organisms including more than 50 endemic species. The northern basin is located in a rural area and has a surface area of 616 km^2 and an average depth of 44 m. The southern basin is located in urban area and has a surface area of 58 km^2 and an average depth of 3.5 m. The waters in the northern basin flow into the southern basin and flow out through the Seta River. The residence time of water is estimated to be 5.5 y for the northern basin and 0.04 y for the southern basin. Nowadays the northern and southern basins are estimated as mesotrophic and eutrophic, respectively, because of human activity. The lake is an intriguing environment, since one can observe a difference in the progression of eutrophication in the two originally identical basins.

Our observation was carried out from June, 1992 to February, 1995 mainly at stations N1 in the northern basin and S3 in the southern basin (1). We determined the concentrations of arsenate [As(V)], arsenite [As(III)], monomethylarsonic acid [MMAA(V)], monomethylarsonous acid [MMAA(III)], dimethylarsinic acid [DMAA(V)] and dimethylarsinous acid [DMAA(III)] in lake water (2). The concentrations of MMAA(III) and DMAA(III) were low (less than 0.3 nM), and therefore methylarsenicals were treated as MMAA(V+III) and DMAA(V+III). The total arsenic concentration was determined after the organoarsenicals were converted into As(V) by alkaline persulfate oxidation in a Teflon digestion bomb. This value agreed closely with Σ As, the sum of concentrations of As(V), As(III), DMAA(V+III) and MMAA(V+III) . Therefore, these species comprise more than 95% of dissolved arsenicals in Lake Biwa.

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INTERFACE SCIENCE — Separation Chemistry —

Scope of research

Our research activities are concerned in selective complex formation systems (molecular recognition). Major subjects of the research are followings: (1) Design and synthesis of the selective complex formation systems. Ligands (host molecules) that have novel functions in separation of metal ions and guest molecules are designed and synthesized. Their functions are analyzed basing on structures of the ligands and complexes. (2) Biogeochemistry of trace elements in the hydrosphere. Novel analytical methods for trace elements are developed. The behavior of trace elements in the hydrosphere is explored.

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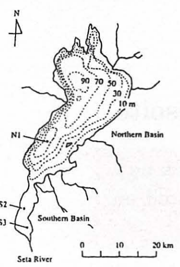

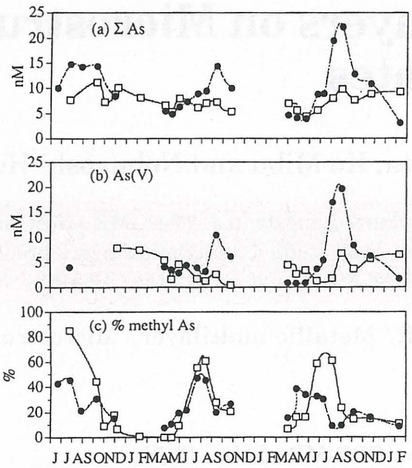

Figure 1. Location of sampling stations.

Figure 2. The seasonal variation of (a) Σ As, (b) As(V), (c) percentage of methylarsenicals, in the epilimnion. Open squares and filled circles show the data for the northern and southern basins, respectively.

Fig. 2 shows the seasonal change of arsenicals in the epilimnion. The Σ As in the southern basin was increased by 2-4 times in summer, while it was nearly constant in the northern basin. The enhancement was caused by the increase of As(V). Because there is no seasonal external source of As(V), it seems that the source is accumulated arsenicals in the sediments of the southern basin. Arsenicals are adsorbed onto ferro-manganese oxides in oxic lake water and settle to the bottom. When the ferromanganese oxides are reduced under anoxic condition, arsenicals are redissolved. Dissolved oxygen (DO) is normally never depleted in the hypolimnion in the shallow southern basin even in summer. S3 is located at a dredged area (0.25 km^2, depth 13 m), where the water is stratified from June to September and DO is totally depleted in the hypolimnion. Thus, we could observe the anoxic process in a water column which normally occurs in the depth of the sediment. The vertical profiles of chemical species obtained at S3 on 30 August 1994 are shown in Fig. 3. DO was depleted below 8 m, and the concentrations of Mn, Fe, As(V) and As(III) increased toward the bottom. This indicates that ferromanganese oxides were reductively dissolved and released arsenicals. Phosphate, which is a chemical analogue of As(V), was concurrently released from the sediment.

The summer enhancement of ΣAs in the epilimnion was also observed at other stations in the southern basin, such as S2 at the center of the basin. The maximum of ΣAs was largest in 1994, when there was an unusually hot and dry summer. The water level of the lake fell to -123 cm on 15 September, which was the lowest level ever observed, and a large amount of algae withered around shallows of the southern basin. Since the large biomass in the basin promotes development of anoxic condition in the depth of the sediment, the release of arsenicals similar to that observed in the hypolimnion of S3 was apparently widespread in pore water of the sediment. Although most of arsenicals is adsorbed onto the

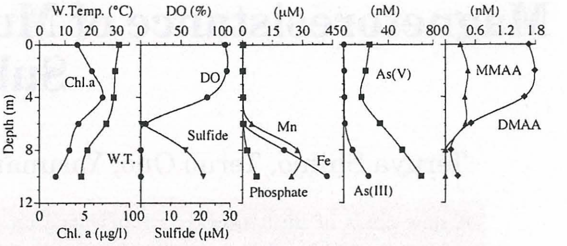

Figure 3. The vertical depth profiles of dissolved concentration of chemical species and water temperature at S3 on 30 August, 1994.

ferro-manganese oxides formed at the oxic surface of the sediment, some of them is supplied to the lake water. The supply was large in 1994, when local anoxic conditions were extensively developed in the surface sediments.

The change in speciation of arsenicals mainly occurred in the euphotic zone. As(V) was distributed uniformly through the water column in winter and its concentration decreased in the epilimnion in summer. As(III) increased during spring and fall blooms, while DMAA(V+III) became dominant in summer. The seasonal variation is probably a common feature of lakes and seas in the temperate zone. The speciation change is a result of the arsenic metabolism of phytoplankton and other aquatic organisms. The biomass in the southern basin is much larger than that in the northern basin as indicated by the concentration of chlorophyll a and transparency. It was reported that in 1993 the mean density of phytoplankton was 950 and 2500 cells/ml at the centers of the northern and southern basin, respectively. The southern basin contained more kinds of plankton species in addition to almost all dominant species observed in the northern basin. Although higher productivity is expected in the southern basin, the concentrations of As(III) and methylarsenicals produced through the arsenic metabolism were comparable to those in the northern basin. The percentage of methylarsenicals was low in the southern basin (Fig. 2). A culture experiment has revealed that uptake of As(V) by marine algae is inhibited competitively by phosphate at concentrations on the order of µM. While the phosphate was nearly depleted in the epilimnion in both the basins, the total budget of phosphorus was larger in the southern basin. The large load of phosphorus may have decreased the arsenic metabolism efficiency of phytoplankton in the southern basin. Another possibility is that degradation of organoarsenicals by bacteria may have been rapid in the southern basin because of its large population.

The eutrophication changed the concentration and speciation of the trace element in the water, and the change may further affect the ecosystem in the lake.

References

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